

AD-A248 029



2

OFFICE OF NAVAL RESEARCH

CONTRACT NO. N000 14-89-J-1849

R & T Code 4134005

TECHNICAL REPORT NO. 20

THE CRYSTAL GROWTH AND CHARACTERIZATION OF THE  
SOLID SOLUTIONS  $(\text{ZnS})_{1-x}(\text{CuMS}_2)_x$

by

Y. R. Do, K. Dwight and A. Wold

Submitted to

Chemistry of Materials



March 24, 1992

Brown University  
Department of Chemistry  
Providence, Rhode Island, 02912

Reproduction in whole or in part is permitted for any purpose of the  
United States Government.

This document has been approved for public release and sale; its  
distribution is unlimited

92 3 30 050

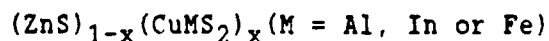
92-07963



## REPORT DOCUMENTATION PAGE

1a REPORT SECURITY CLASSIFICATION UNCLASSIFIED			1b RESTRICTIVE MARKINGS	
2a SECURITY CLASSIFICATION AUTHORITY			3 DISTRIBUTION/AVAILABILITY OF REPORT	
2b DECLASSIFICATION/DOWNGRADING SCHEDULE				
4 PERFORMING ORGANIZATION REPORT NUMBER(S) REPORT NO. 20			5 MONITORING ORGANIZATION REPORT NUMBER(S)	
6a NAME OF PERFORMING ORGANIZATION BROWN UNIVERSITY AARON WOLD		6b OFFICE SYMBOL (If applicable)	7a NAME OF MONITORING ORGANIZATION	
6c ADDRESS (City, State, and ZIP Code) DEPARTMENT OF CHEMISTRY, BOX H BROWN UNIVERSITY PROVIDENCE, RI 02912			7b ADDRESS (City, State, and ZIP Code)	
8a NAME OF FUNDING/SPONSORING ORGANIZATION		8b OFFICE SYMBOL (If applicable)	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER	
8c ADDRESS (City, State, and ZIP Code)			10 SOURCE OF FUNDING NUMBERS	
			PROGRAM ELEMENT NO	PROJECT NO
11 TITLE (Include Security Classification) THE CRYSTAL GROWTH AND CHARACTERIZATION OF THE SOLID SOLUTIONS $(\text{ZnS})_{1-x}(\text{CuMS}_2)_x$ M = Al, In or Fe				
12 PERSONAL AUTHOR(S) Y.R. Do, K. Dwight and A. Wold				
13a TYPE OF REPORT Technical	13b TIME COVERED FROM _____ TO _____	14 DATE OF REPORT (Year, Month, Day) March 24, 1992	15 PAGE COUNT	
16 SUPPLEMENTARY NOTATION Submitted to Chemistry of Materials				
17 COSATI CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP		
19 ABSTRACT (Continue on reverse if necessary and identify by block number) Polycrystalline samples of members of the systems $(\text{ZnS})_{1-x}(\text{CuMS}_2)_x$ (M = Al, In or Fe) were prepared by direct combination of the elements. The difference between the solubility characteristics of $\text{Cu}_2\text{MS}_2$ (M = Al, Ga or In) in ZnS and that of $\text{CuFeS}_2$ in ZnS is discussed. Single crystals of members of the systems $(\text{ZnS})_{1-x}(\text{CuMS}_2)_x$ (M=Al, In or Fe) (nominal composition, $x = 0, 0.05, 0.01$ ) have been grown by chemical vapor transport using iodine as the transport agent. They all crystallize with the zinc blende structure. Their IR transmission range is narrower than that observed for pure ZnS, but all, except for the ZnS-CuInS <sub>2</sub> system, still show good transmission in the long wavelength IR range. The addition of small amounts of I-III-VI <sub>2</sub> modifies the hardness and the thermal stability of ZnS.				
20 DISTRIBUTION/AVAILABILITY OF ABSTRACT <input type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS			21 ABSTRACT SECURITY CLASSIFICATION	
22a NAME OF RESPONSIBLE INDIVIDUAL			22b TELEPHONE (Include Area Code)	22c OFFICE SYMBOL

## The Crystal Growth and Characterization of the Solid Solutions



Y. R. Do, K. Dwight and A. Wold

Department of Chemistry, Brown University

Providence, Rhode Island 02912

### Abstract

Polycrystalline samples of members of the systems  $(\text{ZnS})_{1-x}(\text{CuMS}_2)_x$  (M = Al, In or Fe) were prepared by direct combination of the elements. The difference between the solubility characteristics of  $\text{CuMS}_2$  (M = Al, Ga or In) in ZnS and that of  $\text{CuFeS}_2$  in ZnS is discussed. Single crystals of members of the systems  $(\text{ZnS})_{1-x}(\text{CuMS}_2)_x$  (M = Al, In or Fe) (nominal composition,  $x = 0, 0.05, 0.01$ ) have been grown by chemical vapor transport using iodine as the transport agent. They all crystallize with the zinc blende structure. Their IR transmission range is narrower than that observed for pure ZnS, but all, except for the ZnS-CuInS<sub>2</sub> system, still show good transmission in the long wavelength IR range. The addition of small amounts of I-III-VI<sub>2</sub> modifies the hardness and the thermal stability of ZnS.

### Introduction

ZnS has been studied extensively because it offers a variety of unique device applications. ZnS crystallizes with the cubic zinc blende structure

below 1020°C and with the hexagonal wurtzite structure above this phase transition temperature. The ternary chalcogenides,  $\text{CuMS}_2$  ( $\text{M} = \text{Al, Ga, In or Fe}$ ) crystallize with the chalcopyrite structure, which is closely related to the cubic zinc blende structure. In the chalcopyrite structure, there is an ordering of  $\text{Cu(I)}$  and  $\text{M(III)}$  ( $\text{M} = \text{Al, Ga, In or Fe}$ ) which results in a doubling of the c-axis. There have been relatively few studies (1-4) carried out on the preparation and characterization of solid solutions formed between  $\text{ZnS}$  and  $\text{CuMS}_2$  ( $\text{M} = \text{Al, Ga, In or Fe}$ ). Apple (1) and Robbins et al. (2), have investigated the extent of the solid solutions  $(\text{ZnS})_{1-x}(\text{CuMS}_2)_x$  ( $\text{M} = \text{Al, Ga or In}$ ) and have determined their optical properties. It was noted that the ternary chalcopyrites,  $\text{CuMS}_2$  ( $\text{M} = \text{Al, Ga or In}$ ), were totally miscible with  $\text{ZnS}$ . In the  $(\text{ZnS})_{1-x}(\text{CuMS}_2)_x$  ( $\text{M} = \text{Al, Ga or In}$ ) systems, the cubic zinc blende structure was the stable structure for substitution of up to 30 mole %  $\text{CuAlS}_2$ , 40 mole %  $\text{CuGaS}_2$  or 50 mole %  $\text{CuInS}_2$ , respectively. Moh (3) and Sugaki et al. (4) have reported the phase relations between  $\text{ZnS}$  and  $\text{CuFeS}_2$  above 300°C. In the pseudo-binary  $\text{ZnS-CuFeS}_2$  system, the maximum  $\text{CuFeS}_2$  in  $\text{ZnS}$  is approximately 1.6 mole % at 800°C.

$\text{ZnS}$  is used as an IR window material because of its wide transmission range in the far infrared. However,  $\text{ZnS}$  is soft, which limits its suitability for some applications. Previous work (5), reported that single crystals of members of the system  $(\text{ZnS})_{1-x}(\text{CuGaS}_2)_x$  ( $x=0.053, 0.103$ ) showed good transmission in the far-infrared range and were much harder than  $\text{ZnS}$ . Therefore, it should be possible to modify the properties of  $\text{ZnS}$  using the other chalcopyrites,  $\text{CuMS}_2$  ( $\text{M} = \text{Al, In or Fe}$ ), as components.

The chemical vapor transport method has been widely and conveniently applied to grow single crystals of  $\text{ZnS}$  and  $\text{CuMS}_2$  ( $\text{M} = \text{Al, Ga or In}$ ) (6-9). In a recent study (5), single crystals of the solid solutions formed between  $\text{ZnS}$  and  $\text{CuGaS}_2$ , suitable for characterization, were grown by chemical vapor

transport using iodine as the transport agent. Therefore, this method is extended in this study to grow single crystals of  $(\text{ZnS})_{1-x}(\text{CuMS}_2)_x$  ( $M = \text{Al, In}$  or  $\text{Fe}$ ). Polycrystalline samples were also prepared by the direct combination of zinc, copper, aluminum, indium or iron and sulfur. This study concerns itself with the preparation and characterization of the systems  $(\text{ZnS})_{1-x}(\text{CuMS}_2)_x$  ( $M = \text{Al, In}$  or  $\text{Fe}$ ) for both powder and single crystal samples. Attention is focused on such problems as the different solubility characteristics between  $\text{CuMS}_2$  ( $M = \text{Al, Ga}$  or  $\text{In}$ ) and  $\text{CuFeS}_2$  in  $\text{ZnS}$  and the magnetic behavior of  $\text{Fe(III)}$  in a tetrahedral site, as well as the IR transmission, thermal stability and hardness of the materials.

## Experimental

### *Preparation of Polycrystalline Samples*

Members of the systems  $(\text{ZnS})_{1-x}(\text{CuMS}_2)_x$  ( $M = \text{Al, In}$  or  $\text{Fe}$ ) were prepared by the following procedure: polycrystalline samples with different compositions were prepared by using stoichiometric amounts of zinc (Gallard and Schlesinger 99.9995%) sublimed prior to use, copper (Johnson Matthey 99.9995%) or iron (Leico 46987) prereduced in  $\text{Ar/H}_2$  (85/15) and sulfur (Gallard and Schlesinger 99.999%). The appropriate weights of the reactants to give a total weight of 1 or 2 g of product were sealed in evacuated 12 mm i.d. x 60 mm silica tubes. In order to complete the reaction between the metal and sulfur without exploding the sample tubes, the tubes were heated to 400, 500, 600 and 700°C and held for 24 hr at each temperature. They were finally heated up to 800°C and held at that temperature for 72 hr. The samples were then ground under a nitrogen atmosphere and reheated for 24 hr (Al, In) or 48 hr (Fe) at 800°C. The samples were intimately mixed after each

For

<input checked="" type="checkbox"/>
<input type="checkbox"/>
<input type="checkbox"/>

on

by

Code

and/or

date



A-1

heat treatment. Finally, the samples were cooled in the furnace to room temperature before removal.

### *Crystal Growth*

Single crystals of ZnS and  $(\text{ZnS})_{1-x}(\text{CuMS}_2)_x$  ( $M = \text{Al, In or Fe}$ ) were grown by chemical vapor transport using iodine as the transport agent. Polycrystalline samples were introduced into a silica tube (14 mm o.d., 12 mm i.d. x 300 mm) which had been previously heated to near its melting point in order to minimize any nucleation sites. The tube was evacuated to  $10^{-5}$  torr and freshly sublimed iodine (Deepwater Chemical Co., Std. ACS reagent 99.9%) was introduced as the transport agent at a concentration of 5 mg/ml. The tube was sealed off and enclosed in a tightly wound Kanthal coil (to even out temperature gradients) and the whole assembly was placed in a three-zone furnace. The crystal growth temperature program consisted of setting the furnace to back transport mode for one day, equilibrating the furnace to the maximum temperature for 3 hr, and finally, cooling the growth zone at  $1^\circ\text{C/hr}$  to the growth temperature (10). Optimum crystal growth for ZnS took place when the charge zone was maintained at  $950^\circ\text{C}$  and the growth zone at  $925^\circ\text{C}$ . The optimum growth conditions for single crystals of  $(\text{ZnS})_{1-x}(\text{CuMS}_2)_x$  ( $M = \text{Al, In or Fe}$ ) are summarized in Table I. The transport process was carried out for one week. The typical sizes of different compositional crystals are also given in Table I. The actual composition of each single crystal of  $(\text{ZnS})_{1-x}(\text{CuMS}_2)_x$  ( $M = \text{Al or In}$ ) was determined from cell parameter measurements of known polycrystalline samples. The compositions of the  $(\text{ZnS})_{1-x}(\text{CuFeS}_2)_x$  single crystals were verified from magnetic measurements of single crystals.

### *Characterization of Products*

X-ray powder diffraction patterns of samples were obtained using a Philips diffractometer and monochromated high intensity  $\text{CuK}\alpha_1$  radiation

( $\lambda = 1.5405 \text{ \AA}$ ). For qualitative phase identification, diffraction patterns were taken over the range  $12^\circ < 2\theta < 80^\circ$  with a scan rate of  $1^\circ 2\theta/\text{min}$ , while cell parameters were determined from scans taken at  $0.25^\circ 2\theta/\text{min}$ . Precise lattice parameters were obtained from the diffraction peaks using a least-squares refinement program which corrects for the systematic errors of the diffractometer.

Single crystals were polished on opposite faces with progressive suspensions of 1, 0.5 and  $0.3 \text{ }\mu\text{m}$  alumina on alpha A polishing cloth (Mark V Laboratory) using a Minimet polisher. Optical measurements were performed at room temperature on a Perkin-Elmer 580 double scanning infrared spectrophotometer. The measurements were carried out in the transmission mode over the range  $2.5 - 50 \text{ }\mu\text{m}$ . Transmission through the sample was normalized to the signal obtained in the absence of the sample.

Microhardness measurements (Knoop indenter) were made on polished single crystals using a Kentron microhardness tester. The results were obtained using a diamond indenter with a 25-g load.

The stability of these compounds toward oxidation was determined by grinding a small crystal and heating the resulting powder in flowing oxygen ( $60 \text{ ml/min}$ ) and monitoring the change in weight during the heating period. The decomposition temperature was determined as the temperature where the weight of the sample began to change.

Magnetic susceptibilities were measured from liquid nitrogen temperature ( $77 \text{ K}$ ) to  $300 \text{ K}$  using a Faraday balance at a field strength of  $10.4 \text{ kOe}$ . Honda-Owens (field dependency) plots were also made and all magnetic susceptibility data were corrected for diamagnetism.

## Results and Discussion

$\text{CuAlS}_2$  and  $\text{CuInS}_2$  crystallize with the same structure as  $\text{CuGaS}_2$  and they show similar chemical and physical properties. Therefore, the characterization of  $(\text{ZnS})_{1-x}(\text{CuMS}_2)_x$  ( $M = \text{Al}$  or  $\text{In}$ ) systems have been analyzed similarly to the  $(\text{ZnS})_{1-x}(\text{CuGaS}_2)_x$  system which was previously reported (5). Polycrystalline samples of  $(\text{ZnS})_{1-x}(\text{CuMS}_2)_x$  ( $M = \text{Al}$  or  $\text{In}$ ) where  $x \leq 0.3$  were prepared directly from the elements. X-ray diffraction analyses indicated that  $(\text{ZnS})_{1-x}(\text{CuMS}_2)_x$  ( $M = \text{Al}$  or  $\text{In}$ ) polycrystalline samples were all single phase with the cubic zinc blende structure. These results are in good agreement with previous studies (1,2) which have reported the extent of the solid solutions  $(\text{ZnS})_{1-x}(\text{CuMS}_2)_x$  ( $M = \text{Al}$ ,  $\text{Ga}$  or  $\text{In}$ ). Because of similarities in structure, unit cell dimensions and bond type, the ternary sulfides  $\text{CuMS}_2$  ( $M = \text{Al}$ ,  $\text{Ga}$  or  $\text{In}$ ) were found to be totally miscible with  $\text{ZnS}$ .

The cell parameters of the polycrystalline samples are plotted as a function of chalcopyrite concentration for  $(\text{ZnS})_{1-x}(\text{CuMS}_2)_x$  ( $M = \text{Al}$  or  $\text{In}$ ) in Fig. 1. At chalcopyrite concentrations less than 30.0 mole %, the cell parameters decrease linearly with increasing amounts of substituted chalcopyrite in the aluminum system, and increase linearly in the indium system in accordance with Vegard's law. The cell parameter data are in good agreement with those reported by previous papers (2,11). The composition of unanalyzed single crystals, which are grown by chemical vapor transport, can be obtained from the linear relationship between the cell parameter and the concentration of substituted chalcopyrite.

Single crystals of  $(\text{ZnS})_{1-x}(\text{CuMS}_2)_x$  ( $M = \text{Al}$  or  $\text{In}$ ) ( $x = 0.05$  or  $0.10$ ) were grown by chemical vapor transport using iodine as the transport agent. All single crystals grown crystallized with the cubic zinc blende structure. The properties of these compounds are summarized in Table II. The results of the



ZnS-CuGaS<sub>2</sub> system were given in a previous paper (5). The compositions of (ZnS)<sub>1-x</sub>(CuMS<sub>2</sub>)<sub>x</sub> (M = Al or In) single crystals were determined by comparing their cell parameters with those obtained from a plot of cell parameter vs composition for the standard polycrystalline materials (Fig. 1). The results of these determinations for (ZnS)<sub>1-x</sub>(CuMS<sub>2</sub>)<sub>x</sub> (M = Al or In) are given in Table II. It can be seen that the actual composition of some of the transported crystals deviated from their nominal composition. Hence, the comparison of single crystal cell parameters with those of known standards is essential for determining composition.

The hardness values, as determined by the Knoop method, are given in Table II. The measured hardness of pure ZnS is 153 Kg/mm<sup>2</sup>, which is in good agreement with previous investigations (12-14). It is noted that the hardness values of the crystals containing chalcopyrite substitution show a significant increase compared to the value of the pure end member. From previous studies (9, 15), it has been reported that chalcopyrites (I-III-VI<sub>2</sub>) are much harder than II-VI compounds and that the hardness of chalcopyrites decreases from CuAlS<sub>2</sub> to CuInS<sub>2</sub>. The substitution of CuAlS<sub>2</sub> results in a relatively larger increase in the hardness of ZnS than an equivalent substitution of CuGaS<sub>2</sub> or CuInS<sub>2</sub>. These results are in agreement with those reported by He et al. (15) in which the measured value of the hardness of CuAlS<sub>2</sub> is greater than that of CuGaS<sub>2</sub>. Shay and Wernick (9) have speculated that as the atomic number increases in the same family, atoms are more polarizable and hence a decrease in the measured hardness would be anticipated. Even at the low concentrations of chalcopyrite substituted for ZnS in this study, the effective increase in the hardening by CuAlS<sub>2</sub> can be observed (Table II).

The IR transmission data are also summarized in Table II. The results indicate that pure ZnS transmits in the range of 1.5 - 14  $\mu$ m, which is in good agreement with previous reports (12-14). CuAlS<sub>2</sub> causes a marked decrease in

the upper end of the transmission of ZnS and CuGaS<sub>2</sub> does narrow the transmission range particularly at the low end. However, these materials still show good transmission in the long wavelength IR range. In the range of 2.5 - 50  $\mu$ m, CuInS<sub>2</sub> reduces the magnitude of IR transmission by less than 30 %. The thermal stability data, taken in a flowing oxygen atmosphere, show that the chalcopyrites CuAlS<sub>2</sub> and CuGaS<sub>2</sub> increase the decomposition temperatures of pure ZnS (Table II). For the ZnS-CuInS<sub>2</sub> systems, the onset temperature of decomposition is lower than that of pure ZnS.

The electrical and optical properties of the CuMS<sub>2</sub> compounds (M = Al, Ga or In) have been reported by Tell et al. (16). In early studies, Shay et al. (17-19) have indicated that many of the electronic properties can be explained if the valence band is assigned considerable d-character. This can result from the hybridization of copper 3d orbitals and anion sp states. In a more recent paper, Jaffe and Zunger (20) have calculated the electronic structure of these ternary chalcopyrite semiconductors. They reported that almost all of the copper d-electrons occupy the upper valence band and there are empty group III metal states in the conduction band. The electronic structure of the upper valence band consists primarily of copper 3d-sulfur 3p hybrid wave functions which interact most strongly for CuAlS<sub>2</sub>. The empty conduction band is composed of unoccupied group III - group VI anion states. The filled group III - group VI anion valence band lies below the copper 3d-sulfur 3p band. It is, therefore, not surprising that CuFeS<sub>2</sub> shows different physical and chemical properties from the other CuMS<sub>2</sub> (M = Al, Ga or In) I-III-VI<sub>2</sub> compounds. CuFeS<sub>2</sub>, chalcopyrite, is the only compound which contains a magnetic ion among these tetrahedrally coordinated semiconductors. With respect to the measured electrical properties, there is little difference between chalcopyrite and the non-magnetic analogs. However, the observed Hall mobility for chalcopyrite of 35 cm<sup>2</sup>/v-sec at 80 K (19) is small, which suggests some effect of the unpaired

iron 3d electrons on the electrical properties. Furthermore, from optical measurements, Goodman and Austin (21, 22) reported that the absorption edge of 0.5 eV for  $\text{CuFeS}_2$  is much smaller than the value of 2.5 eV measured for  $\text{CuGaS}_2$ . The difference in the absorption edge of  $\text{CuFeS}_2$  may also be related to the delocalization of Fe(III) 3d electrons.

The magnetic properties of  $\text{CuFeS}_2$  show the effect much more clearly. Neutron diffraction (23) and static magnetic measurements (19) have shown that  $\text{CuFeS}_2$  is antiferromagnetic with  $T_N = 550^\circ\text{C}$ . The effective magnetic moment associated with  $\text{Fe}(3d^5)$  was only  $3.85 \mu_B$ . This moment cannot be interpreted with an assignment of  $\text{Fe(III)}3d^5$  which would be consistent with Mössbauer studies, which assign iron as a trivalent species (24,25). Finally, it was shown by Sato and Teranishi (26) that for the systems  $\text{CuFe}_x\text{Al}_{1-x}\text{S}_2$  and  $\text{CuFe}_x\text{Ga}_{1-x}\text{S}_2$  the iron 3d electrons are localized when the iron concentration is small, but undergo a transition to the delocalized state at a critical value of x. These results are consistent with those obtained by Saintavit et al. (27) from XANES spectra. They reported that for  $\text{CuFeS}_2$  there is additional strong hybridization of anion 3p and delocalized iron 3d states.

For the system  $(\text{ZnS})_{1-x}(\text{CuFeS}_2)_x$  where  $0.025 \leq x \leq 0.3$ , x-ray diffraction patterns of polycrystalline samples indicated that there were two phases present, namely, the cubic zinc blende structure and the tetragonal chalcopyrite structure. This is consistent with the report by Moh (3) that the maximum solubility of  $\text{CuFeS}_2$  in ZnS was approximately 1.6 mole % at  $800^\circ\text{C}$ . Undoubtedly, the narrow solubility limit of  $\text{CuFeS}_2$  in ZnS is related to their differences in bonding. For  $\text{CuFeS}_2$ , there is at least a partial participation of the iron unpaired 3d electrons with the uppermost sulfur valence bands. This is also consistent with the evidence previously discussed which supports the delocalization of 3d electrons over the bonding bands. Furthermore, the cell dimensions of  $\text{CuFeS}_2$  ( $a = 5.29 \text{ \AA}$ ,  $c = 10.43 \text{ \AA}$ ) are smaller than those of

$\text{CuGaS}_2$  ( $a = 5.36 \text{ \AA}$ ,  $c = 10.49 \text{ \AA}$ ) even though the radius of  $\text{Fe(III)}$  ( $r = 0.49 \text{ \AA}$ ) is larger than that of  $\text{Ga(III)}$  ( $r = 0.47 \text{ \AA}$ ). This is consistent with the concept of increased metal-sulfur bonding in  $\text{CuFeS}_2$  resulting from partial delocalization of  $\text{Fe(III)}$  3d electrons and admixture with anion p-states.

The composition of  $(\text{ZnS})_{.984}(\text{CuFeS}_2)_{.016}$  single crystals grown by chemical vapor transport was determined by magnetic measurements. The phase crystallized with the zinc blende structure. Magnetic susceptibility measurements were made as functions of both field and temperature. Two separate crystals were measured and showed paramagnetic behavior without any field dependency at either room temperature or at liquid nitrogen temperature. The reciprocal magnetic susceptibility of  $(\text{ZnS})_{.984}(\text{CuFeS}_2)_{.016}$  is plotted versus temperature in Fig. 2 and shows Curie-Weiss behavior with a Weiss constant of  $-55 \text{ K}$ . The composition was calculated by comparing the magnetic susceptibility values at room temperature with those obtained by assuming a spin-only moment (5.9 BM) of the  $\text{Fe(III)}$  ions (Table II). It can be seen that crystals grown from the charge containing  $\text{CuFeS}_2$  to  $\text{ZnS}$  ratio of 10/90 gave a  $\text{CuFeS}_2$  content of 1.6 mole %. This composition is the solubility limit of  $\text{CuFeS}_2$  in  $\text{ZnS}$  single crystals at the growth conditions used. This solubility limit is in agreement with that reported by Moh (3).

The properties of  $(\text{ZnS})_{.984}(\text{CuFeS}_2)_{.016}$  single crystals are summarized in Table II. They give the same IR transmission at the long wavelength end, but there appears to be a cut off at  $5.0 \text{ }\mu\text{m}$ . The microhardness and thermal stability data show that  $\text{CuFeS}_2$  increases the hardness of pure  $\text{ZnS}$  and decreases the decomposition temperature.

## Acknowledgments

This research was partially supported by the Office of Naval Research and by the National Science Foundation, Contract No. DMR 8901270.

## References

1. E. F. Apple, J. Electrochem. Soc. 105, 251 (1958).
2. M. Robbins and M. A. Miksovsky, J. Solid State Chem. 5, 462 (1972).
3. G. H. Moh, Chem. Erde. 34, 1 (1975).
4. S. Kojima and A. Sugaki, Mineralogical J. 12, 15 (1984).
5. Y. R. Do, R. Kershaw, K. Dwight and A. Wold, in press.
6. H. Hartmann, J. Crystal Growth 42, 144 (1977).
7. E. Kaldis, J. Phys. Chem. Solids 26, 1701 (1965).
8. W. N. Honeyman, J. Phys. Chem. Solids 30, 1935 (1969).
9. J. L. Shay and J. H. Wernick, "Ternary Chalcopyrite Semiconductor: Growth, Electronic Properties and Applications," Pergamon Press, New York (1975).
10. R. Kershaw, M. Vlasse, A. Wold, Inorg. Chem. 6, 1599 (1967).
11. P. C. Donohue and P. E. Bierstedt, J. Electrochem. Soc. 121, 327 (1974).
12. P. Wu, R. Kershaw, K. Dwight and A. Wold, Mat. Res. Bull. 24, 49 (1989).
13. J. DiCarlo, M. Albert, K. Dwight and A. Wold, J. Solid State Chem. 87, 443 (1990).

14. C-M. Niu, R. Kershaw, K. Dwight and A. Wold, J. Solid State Chem. 85, 262 (1990).
15. X-C. He, H-S. Shen, P. Wu, K. Dwight and A. Wold, Mat. Res. Bull. 23, 799 (1988).
16. B. Tell, J. L. Shay and H. M. Kasper, J. Appl. Phys. 43, 2469 (1972).
17. J. L. Shay and H. M. Kasper, Phys. Rev. Lett. 29, 1162 (1972).
18. J. L. Shay, B. Tell, H. M. Kasper and L. M. Schiavone, Phys. Rev. B, 5, 5003 (1972).
19. J. L. Shay, B. Tell, H. M. Kasper and L. M. Schiavone, Phys. Rev. B, 7, 4485 (1973).
20. J. E. Jaffe and A. Zunger, Phys. Rev. B, 28, 5822 (1983).
21. C. H. L. Goodman and R. W. Douglas, Physica 20, 1107 (1954).
22. I. G. Austin, C. H. L. Goodman and A. E. Pengelly, J. Electrochem. Soc. 103, 609 (1956).
23. G. Donnay, L. M. Corliss, J. D. H. Donnay, N. Elliot and J. M. Hastings, Phys. Rev. 112, 1917 (1958).
24. E. Frank, Nuovo Cemento B, 63, 407 (1968).
25. D. Raj, K. Chandra and S. P. Puri, J. Phys. Soc. Japan 24, 39 (1968).
26. K. Sato and T. Teranishi, Jpn. J. Appl. Phys. 19, 101 (1980).
27. Ph. Saintavit, J. Petiau, A. M. Flank, J. Ringeissen and S. Lewonczuk, Physica B, 158, 263 (1989).

TABLE I

Growth Conditions and Crystal Size  
for Single Crystals of  $(\text{ZnS})_{1-x}(\text{CuMS}_2)_x$  (M = Al, In or Fe)

	Nominal Comp. (x)	Charge Temp. (°C)	Growth Temp. (°C)	Crystal Size (mm)
	0.00	950	925	10 x 6 x 2
M = Al	0.05*	870	830	3 x 3 x 2
	0.10*	880	850	3 x 7 x 2
M = In	0.05*	840	810	4 x 3 x 1
	0.10*	840	810	10 x 5 x 1
M = Fe	0.10*	840	800	13 x 6 x 1

\* nominal composition

TABLE II

Properties of  $(\text{ZnS})_{1-x}(\text{CuMS}_2)_x$  (M = Al, Ga, In or Fe) Single Crystals

	Nominal comp. (x)	Crystal comp. (x)	Cell parameter (Å)	Knoop hardness (Kg/mm <sup>2</sup> )	Decomp. temp. (°C)	IR Trans. Range (μm)
	0.0	0.0	5.410(2)	153(10)	570	2.5 - 14
M = Al	0.05	0.027	5.407(2)	206(20)	580	4.0 - 10
	0.10	0.069	5.400(2)	275(35)	595	4.0 - 10
M = Ga <sup>a</sup>	0.05	0.053	5.403(2)	250(10)	670	4.5 - 13
	0.10	0.103	5.397(2)	298(20)	680	4.5 - 13
M = In	0.05	0.051	5.422(2)	211(20)	480	-----*
	0.10	0.105	5.433(2)	254(20)	450	-----*
M = Fe	0.10	0.016	5.412(2)	226(15)	530	5.0 - 14

#Reference (5)

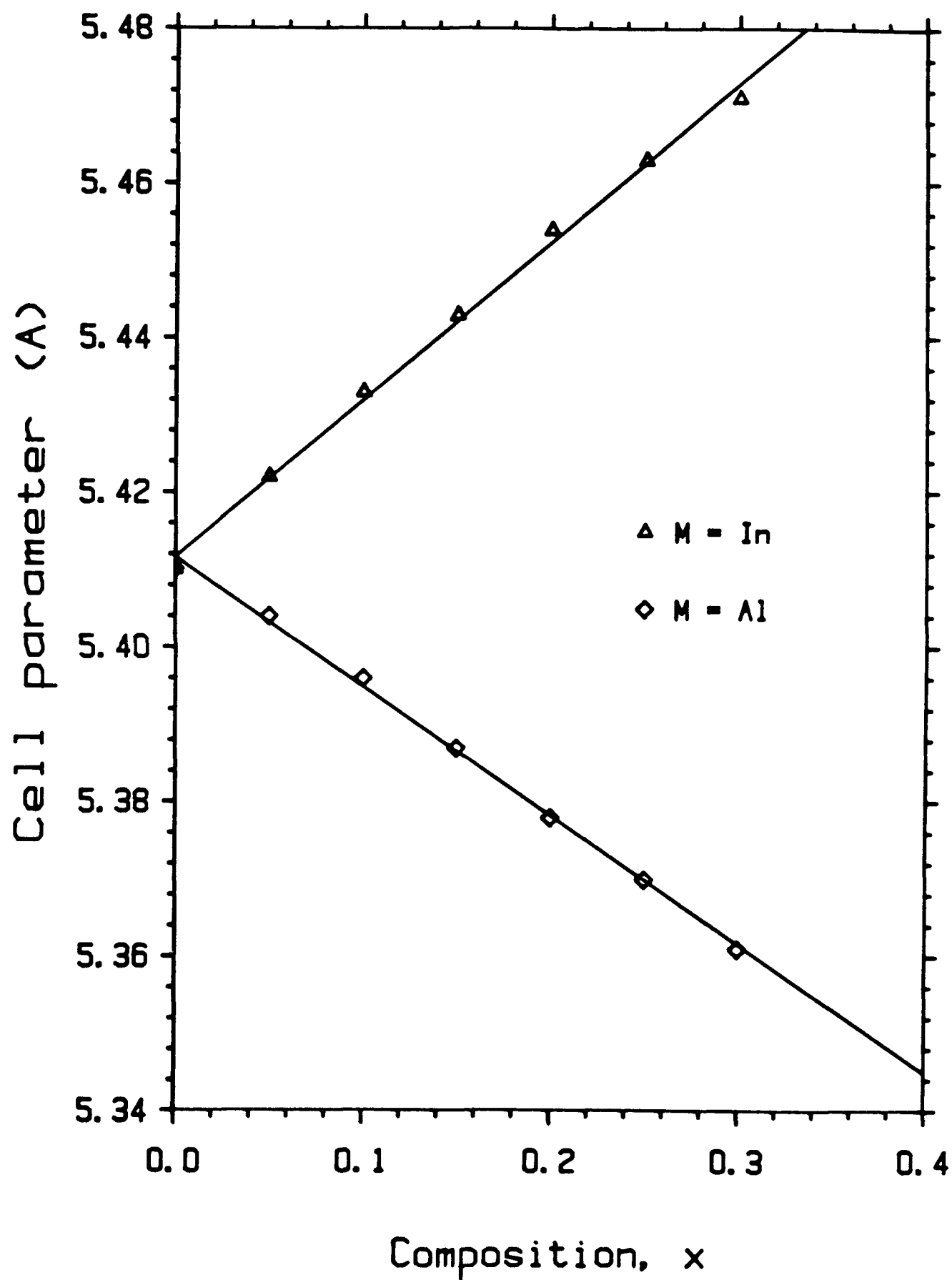
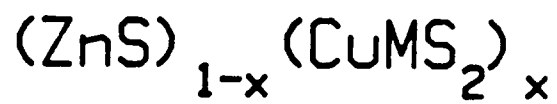
\*The transmission of single crystals with 0.01 cm thickness is less than 30% in the range of 2.5 - 50 μm.



Figure Caption Sheet

Fig. 1. Variation of cell parameter with  $\text{CuAlS}_2$  and  $\text{CuInS}_2$  composition in  $(\text{ZnS})_{1-x}(\text{CuMS}_2)_x$  ( $M = \text{Al, or In}$ ).

Fig. 2. Variation of magnetic susceptibility with temperature for a single crystal of  $(\text{ZnS})_{.984}(\text{CuFeS}_2)_{.016}$ .



$\chi_{\text{corr}}^{-1} (10^{-3} \text{emu/mol sample})^{-1}$

(ZnS) .984 (CuFeS<sub>2</sub>) .016

